Depression of Glass Transition Temperatures of Polymer Networks by Diluents

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The slope of the HDPP line, γ_S, is then calculated as

$$\gamma_S \equiv \left.\frac{\delta w_3}{\delta w_2}\right|_{S=0} = -\frac{(\partial S/\partial w_2)_{w_3}}{(\partial S/\partial w_3)_{w_2}} \quad \text{(A1-2)}$$

with the result given in eq 16.

At $S = 0$, the function ψ of eq 5 is simply

$$\psi(\gamma_\chi) = r_z\frac{r_{z+1} - r_w}{r_z - r_w} \quad \text{(A1-3)}$$

Substitution from eq 2 and 15 for r's and the inversion of the function then yield eq 17 for the direction of the χ_c contour lines at the HDPP line.

Appendix II

Assume for a while that the HDPP line can indeed exist as a closed loop inside the triangle of polymer compositions.

The direction of an HDPP line at a particular point for a given system is a function of only r_z; this is apparent from eq 16 if r_{z+1} is expressed in terms of r_z from the condition $S = 0$. Then at all points of intersection of the HDPP line with a given r_z line running through the loop (at least two for each such r_z line—one entry and one exit), the direction of the HDPP line γ_S would have to be identical. This requirement, however, cannot be satisfied. For instance, the two points of intersection A′ and A″ of Figure 7, infinitesimally close to the tangential point B, are by definition on the same side of the tangential r_z line b. Since the HDPP line is continuous, however, it is bound to have different slopes at points A′ and A″, although both points arise as points of intersection with the same r_z line a.

This proves that no r_z line can form a tangent to the HDPP line and, consequently, that the HDPP line cannot exist as a closed loop entirely contained within the physically significant triangle of compositions where $w_i > 0$, $i = 1$, 2, and 3.

Appendix III

We wish to prove the equivalence of two interpretations of the triple critical point in quaternary systems: (i) as an extremal point of the HDPP line, i.e., a point where the slopes of the HDPP line and of a χ_c contour line are identical (cf. eq 16 and 17)

$$\gamma_S = \gamma_{\chi,S} \quad \text{(A3-1)}$$

(ii) as a point of the HDPP line where (cf. eq 18)

$$Z = 0 \quad \text{(A3-2)}$$

Since the two conditions contain variables of different nature, the compositions w_2 and w_3 of $\gamma_{\chi,S}$ and the average r_{z+2} of Z are first expressed in terms of r_1, r_2, and r_3 and the averages r_z and r_{z+1}, with the result

$$\gamma_{\chi,S} = -\frac{\Delta r_2}{\Delta r_3}\,\frac{r_z(r_{z+1} - r_1 - r_2) + r_1r_2}{r_z(r_{z+1} - r_1 - r_3) + r_1r_3}\,\frac{r_z(r_{z+1} - R) + r_1r_3 + r_2r_3}{r_z(r_{z+1} - R) + r_1r_2 + r_2r_3} \quad \text{(A3-3)}$$

$$Z \propto Rr_zr_{z+1} - Pr_z - r_z^2(10r_{z+1} - 15r_z + 6) + T \quad \text{(A3-4)}$$

where

$$R = r_1 + r_2 + r_3$$

$$P = r_1r_2 + r_2r_3 + r_1r_3$$

$$T = r_1r_2r_3$$

Using these two forms, one can prove after some tedious rearrangements that the above conditions (i) and (ii) are indeed equivalent.

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(11) The parameter χ is plotted in Figures 1 and 2 in the negative sense (i.e., increasing downward) in order to make the graphs qualitatively similar to temperature diagrams typical for solutions of polymers in poor solvents, where $d\chi/dT < 0$. The same sign convention is used for discussion of quaternary systems. Hence, a minimum of the critical line corresponds to a maximum value of the parameter χ.
(12) A critical point of multiplicity n can be defined in terms of derivatives of the CPC function $F(\sigma,\phi)$ (see, e.g., eq 7 of ref 10) at the critical point by the condition $(\partial^k F/\partial\sigma^k)_{\phi,\sigma=0} = 0$; $k = 0$, 1, ..., $n + 2$.[10]
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Depression of Glass Transition Temperatures of Polymer Networks by Diluents

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ABSTRACT: A classical thermodynamic theory is used to derive expressions for the depression of the glass transition temperature T_g of a polymer network by a diluent. The enhanced sensitivity of T_g in cross-linked systems to small amounts of diluent is explained. Predictions of the theory are in satisfactory agreement with the experimental values of a particular polymer network/diluent system.

Introduction

Some years ago Couchman and Karasz[1] presented a classical thermodynamic analysis of the effect of composition on glass transition temperatures of binary mixtures. This theory has been used to describe successfully the glass transition temperature of compatible polymer blends.[2] Recently,[3-5] this was also applied to polymer/diluent systems, proving the ability of the theory to deal with a

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Table I

system	T_{g_1}, K	T_{g_2}, K	ΔC_{p_1}, J/(g K)	ΔC_{p_2}, J/(g K)	$(dT_g/dx_2)_{x_2=0}$, K/% dil exptl	calcd
PS/ethylbenzene[a]	385	113	0.28	0.7	6.5	6.7
PS/styrene[b]	378	119	0.27	0.77	7	7.4
PS/hexamer[b]	378	255	0.27	0.41	2	1.9
epoxy/water[b]	412	134	0.35	1.94	15	15.4
epoxy/methanol[b]	412	104	0.35	0.81	7.5	7.1
epoxy/ethanol[b]	412	102	0.35	0.67	5	5.9
epoxy/butanol[b]	412	184	0.35	0.51	2	3.3

[a] Reference 7. [b] References 3 and 4.

wide variety of systems. An even more challenging situation arises by considering the glass transition temperature depression of polymer networks by diluents. Former applications of the Couchman–Karasz approach to these systems, however, invariably overestimated the plasticization effect.[3-5] It is the purpose of this paper to establish that these systems are also well within the scope of the theory.

Compositional Variation of T_g

Couchman and Karasz[1] treated the glass transition as a quasi-second-order phase transition in the Ehrenfest sense. Using the characteristic continuity of the total system entropy, they derived an expression for the glass transition temperature T_g of a binary mixture as a function of the pure component properties:

$$x_1\int_{T_{g_1}}^{T_g}(C_{p_1}^{\,l} - C_{p_1}^{\,g})\,d\ln T + x_2\int_{T_{g_2}}^{T_g}(C_{p_2}^{\,l} - C_{p_2}^{\,g})\,d\ln T + \Delta S_m^{\,l} - \Delta S_m^{\,g} = 0 \quad (1)$$

In this relationship x_i, T_{g_i}, $C_{p_i}^{\,l}$, and $C_{p_i}^{\,g}$ (i = 1 and 2) denote the mole fraction, the glass transition temperature, and the specific heat of the liquid and the glassy state of components 1 and 2, respectively. $\Delta S_m^{\,l}$ and $\Delta S_m^{\,g}$ are the excess entropies of mixing just above and below T_g. Couchman[2] argued that the difference $\Delta S_m^{\,l} - \Delta S_m^{\,g}$ may, in general, be neglected for compatible polymer blends, because both $\Delta S_m^{\,l}$ and $\Delta S_m^{\,g}$ are very small. For polymer/diluent systems both terms will be much larger. Nevertheless, their difference may still be negligible because it is known[2] to be zero for ideal and regular solutions. Deviations may be expected in some cases. In particular, as indicated by Angell et al.,[6] any specific interaction between polymer and solvent will most probably result in a greater than normal change of T_g with x_2, whereas a flattening out of the T_g composition dependence may be caused by imminent phase separation. The latter is of considerable importance for polymer/diluent systems, since nearly all these systems show phase separation upon cooling (UCST) and upon heating (LCST). Depending on the system under investigation, either of these phase separation phenomena may interfere with the glass transition. However, in our treatment we will, unless otherwise indicated, assume that the excess entropy of mixing difference can be neglected. Equation 1, therefore, reduces to

$$x_1\int_{T_{g_1}}^{T_g}\Delta C_{p_1}\,d\ln T + x_2\int_{T_{g_2}}^{T_g}\Delta C_{p_2}\,d\ln T = 0 \quad (2)$$

where $\Delta C_{p_i} \equiv C_{p_i}^{\,l} - C_{p_i}^{\,g}$ (i = 1 and 2).

We are interested in binary mixtures in which the first component is a polymer and the second component is a low molecular weight solvent. In that case the mixture T_g satisfies $T_{g_2} < T_g < T_{g_1}$. Any application of eq 2 therefore requires knowledge of the extrapolated values of the specific heat of the glassy state of the diluent to temperatures above T_{g_2} and of the specific heat of the liquid state of the polymer to temperatures below T_{g_1}. A way to solve this problem is to assume that as a first approximation ΔC_{p_1} and ΔC_{p_2} are independent of temperature. This has proven to be a very good approximation for some polymer blends,[2] principally because the difference between the pure component glass transition temperatures is rather small. For polymer/diluent systems, this would be a very questionable approach since, in this case, the T_g's are usually several hundreds of degrees apart. In order to solve this problem we note first that our main interest is the depression of the glass transition temperature due to small amounts of diluent. In this limit one obtains by differentiating eq 2

$$(dT_g/dx_2)_{x_2=0} = -\frac{T_{g_1}}{\Delta C_{p_1}}\int_{T_{g_2}}^{T_{g_1}}\Delta C_{p_2}\,d\ln T \quad (3)$$

where now ΔC_{p_1} is the incremental change in specific heat at T_{g_1}. This expression shows that the depression due to a small amount of diluent is determined by the temperature dependence of ΔC_{p_2}. The temperature dependence of ΔC_{p_1} plays no role in this limit. Heretofore, eq 3 has nearly always been used assuming ΔC_{p_2} to be independent of temperature, which resulted in a greater glass transition temperature depression than observed. A more accurate approximation[6] is given by ΔC_{p_2} = constant/T, where the constant is determined by the value of ΔC_{p_2} at T_{g_2}. Substituting this into eq 3 results in

$$(dT_g/dx_2)_{x_2=0} = -\frac{\Delta C_{p_2}}{\Delta C_{p_1}}(T_{g_1} - T_{g_2}) \quad (4)$$

where from now on ΔC_{p_1} and ΔC_{p_2} are the incremental changes in specific heat at T_{g_1} and T_{g_2}, respectively.

Equation 4 has been applied to a number of systems for which experimental results were obtained at our laboratory. Table I shows that it gives a good account of the observed behavior. It should be noted that the epoxys are actually lightly cross-linked networks. The results in Table I support the correctness of the approximations involved in this treatment: the inverse proportionality to temperature of the extrapolated incremental change in specific heat of the diluent and the smallness of the difference $\Delta S_m^{\,l} - \Delta S_m^{\,g}$.

Effect of Cross-Linking

Introducing cross-links in a polymer system will obviously not have any influence on the pure component properties of the diluent. The excess entropies of mixing $\Delta S_m^{\,l}$ and $\Delta S_m^{\,g}$, however, will change. Their difference may become important if the cross-linked system interacts, *due to the cross-links*, strongly with the diluent. We will consider only networks for which the change in chemical composition that accompanies the introduction of cross-

Table II[a]

% DVB (w/w)	T_{g_1}, K	ΔC_{p_1}, J/(g K)	$(dT_g/dx_2)_{x_2=0}$, K/% dil	
			exptl	calcd
0	385	0.283	6.5	6.7
5	390.3	0.252	6.5	7.7
21.0	415.6	0.200	8	10.6
35.7	444.9	0.095	10	24.5

[a] Experimental data; see ref 7.

links can be ignored. An obvious example is given by styrene/divinylbenzene cross-linked polymers. The only difference between this network and pure polystyrene is that some of the free benzene rings in polystyrene are joined to a neighboring chain by normal covalent bonds. As a result both ΔS_m^l and ΔS_m^g will for a particular diluent diminish, and it seems even more likely that their difference is negligible. This will also be the case for a number of other polymer network/diluent systems. To illustrate this, we consider first an ideal or a regular solution of a non-cross-linked polymer and a solvent. The entropy of mixing of such a system is given by

$$\Delta S_m = -\phi_1/p_1 \ln \phi_1 - \phi_2 \ln \phi_2 \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of the polymer, with a degree of polymerization p_1, and the solvent, respectively. For an ideal polymer network and a diluent this becomes[8]

$$\Delta S_m = -\phi_2 \ln \phi_2 + \Delta S_{el} \quad (6)$$

where ΔS_{el} represents the entropy change associated with the change in configuration of the network. Since ΔS_{el} is negative, it is clear that cross-linking reduces the entropy of mixing. Moreover, in this simple example ΔS_m is solely configurational and therefore continuous at T_g.

In order to compare predicted depressions of the glass transition temperature based on eq 4 with observed ones, one has to know the glass transition temperature T_g and the incremental change in specific heat ΔC_{p_1} as a function of the degree of cross-linking. DSC measurements of cross-linked samples show a pronounced widening of the transition region due to the fact that the meshes are of different lengths. The chain units in the longest mesh are the first to be activated in the sense of cooperative motion followed by the remaining ones. As the glass transition temperature one should take the temperature at which the great mass of chain units becomes activated. Consequently, the most appropriate way to determine the glass transition temperature of a network from a DSC scan is by the so-called midpoint method.

Table II contains the glass transition temperatures determined in this manner and the incremental change in specific heat for three different degrees of cross-linking of styrene/divinylbenzene networks.[7] Also included are the experimental and the predicted values of $(dT_g/dx_2)_{x_2=0}$, using ethylbenzene, which is known to be a good solvent for polystyrene,[9,10] as a diluent. The latter are obtained from eq 4 using data of Tables I and II. As has been noted previously,[3-5] there is an increasing discrepancy between observed and predicted depressions with increasing degree of cross-linking. This has also been noticed for a number of other polymer network/diluent systems.[3]

So far, this failure has been ascribed to the inadequacy of the assumptions involved in the derivation of the expression for dT_g/dx_2. However, as pointed out before, there is no reason to believe that approximations which are apparently valid for pure polystyrene/ethylbenzene mixtures will cease to be valid for styrene/divinylbenzene cross-linked samples. We will offer a simple solution to this problem.

The overestimation of $(dT_g/dx_2)_{x_2=0}$ is, in general, due to a strong decrease of ΔC_{p_1} with increasing degree of cross-linking. Each cross-link forces two chains to come in close contact. Cross-linking is therefore equivalent to the introduction of strong attractive interaction between different chains. This leads to a higher glass transition temperature. Moreover, this linking of various chain units by means of normal valency bonds reduces the number of units capable of being thermally activated, that is, capable of carrying out micro-Brownian or wriggling movements.[11] Only the chain units with benzene rings attached to them that are not cross-linked can in principle rotate around the bent valency bonds of the chain. However, measurements of Uberreiter and Kanig[11] on styrene/divinylbenzene networks show that, for less than four carbon atoms between two successive cross-links, thermal activation of that part of the network is also almost impossible. In general, ΔC_{p_1} becomes vanishingly small at high degrees of cross-linking.[3-5] The measured incremental change in specific heat represents only the activation of those units that are capable of rotating around the valency bonds of the chain. We will as a first approximation assume that they have the same number of degrees of freedom, which are frozen in at T_g, as the units in the un-cross-linked chain. The observed depression of the glass transition temperature by a diluent is determined by these units.

Let $f^{act}(X)$ denote the fraction of chain units capable of being activated for a degree of cross-linking X. The incremental change in specific heat per mole of units capable of being activated $\Delta C_{p_1}^{act}(X)$ is then given by

$$\Delta C_{p_1}^{act}(X) = \Delta C_{p_1}(X)/f^{act}(X) \quad (7)$$

where $\Delta C_{p_1}(X)$ is the experimental value of the incremental change in specific heat per mole of chain units. Equation 4 for the depression of the glass transition temperature becomes accordingly

$$(dT_g(X)/dx_2)_{x_2=0} = \frac{\Delta C_{p_2}[T_{g_1}(X) - T_{g_2}]}{\Delta C_{p_1}^{act}(X)} \quad (8)$$

The fraction of the chain units between two cross-links that are capable of being activated depends on the distance between the cross-links. For styrene/divinylbenzene networks, for instance, this fraction drops to zero for distances of less than four carbon atoms. Uberreiter and Kanig showed that for a low degree of cross-linking the fraction of excluded units is approximately equal to the fraction of divinylbenzene units. For larger degrees of cross-linking the number of excluded units increases much faster. A way to obtain an approximate value for this number is to assume that the incremental change in specific heat $\Delta C_{p_1}^{act}(X)$ is independent of the degree of cross-linking. A similar procedure is followed in the study of melting point depression of cross-linked systems.[12] This melting point depression is a result of a reduction of the concentration of segments of length suitable for crystallization. One obtains a value for the concentration of chain units prevented from crystallization by considering the heat of fusion with increasing cross-link density. If the heat of fusion per mole of crystallizable units is taken to be temperature independent, the number of excluded units follows simply from the measured heat of fusion. In our case the fraction of units participating in the glass transition would then be given by

$$f^{act}(X) = \Delta C_{p_1}(X)/\Delta C_{p_1}(X = 0) \quad (9)$$

and eq 8 reduces to

$$[dT_g(X)/dx_2]_{x_2=0} = \frac{\Delta C_{p_2}}{\Delta C_{p_1}(X=0)}[T_{g_1}(X) - T_{g_2}] \quad (10)$$

The increase of the depression of T_g by a small amount of diluent with increasing cross-linking would then exclusively be the result of the increase of $T_{g_1}(X)$. This is, however, an oversimplification. The incremental change in specific heat per mole of units capable of being activated does depend on the freezing-in temperature and we will consider this in more detail in the next section.

Incremental Change in Specific Heat

Studies of statistical mechanical properties of polymer systems are usually based on quasi-lattice models. A polymer molecule is assumed to consist of a number of segments, each occupying one lattice site. The hard-core interaction is simulated by the constraint that a lattice site can only be occupied once. In addition, there are purely intramolecular interactions of the rotational isomeric type. They give rise to one trans and usually two gauche conformations. The latter correspond to links in the chain. Using this lattice model, Gibbs and DiMarzio[13,14] derived an approximate expression for the configurational entropy of a system consisting of polymer molecules and holes. They argued that the configurational entropy per lattice site becomes zero at a certain temperature $T_2 > 0$ and remains zero below T_2. At T_2 there is a second-order phase transition characterized by a discontinuity in specific heat, thermal expansion coefficient, and compressibility. The experimentally observed glass transition T_g is treated as a kinetic process but should ultimately coincide with T_2 at infinitely slow cooling. This model has proven to give a very useful description of a number of phenomena connected with a glass transition.[15] In particular the expression for the discontinuity in specific heat is given by[16,23]

$$\Delta C_{p_1} = n_r R\left\{\left(\frac{\epsilon}{kT}\right)^2 f(1-f) + 4T\Delta\alpha_1(1 - 4.17T\Delta\alpha_1)\right\} \quad (11)$$

where n_r is the number of flexible bonds, R the gas constant, k Boltzmann's constant, T the absolute temperature, ϵ the energy difference between the gauche states and a trans state, f the fraction of bonds in the gauche state, and $\Delta\alpha_1$ the discontinuity in the thermal expansion coefficient. The freezing-in of the conformational population at the glass transition temperature gives rise to the first term between the brackets, whereas the second term is due to the freezing-in of free volume or number of holes.

However, it soon appears that an explanation of the observed ΔC_{p_1} for various polymers, based on this expression, could only be given by making questionable assumptions for either the number of flexible bonds or the number of different gauche states or both.[17,18] The natural choice usually gives too small a value. An additional difficulty arises from the fact that Gujrati[19] recently showed that the predicted second-order phase transition is most likely an artifact due to the approximation involved in evaluating the configurational entropy.

In spite of this, it is believed that the freezing-in of the conformational population is an important part of the glass transition. Roe and Tonelli[20] showed that the sum of this contribution ΔC_1^{conf} and the one associated with the freezing-in of the free volume ΔC_1^{fv} cannot explain all of the observed ΔC_{p_1}. Three other possible contributions suggested by Goldstein[21] are associated with changes with temperature of vibrational frequencies, anharmonicity, and number of groups participating in secondary relaxations. Analyzing data obtained by Chang et al., he concludes that in most cases the larger contribution is due to either anharmonicity or secondary relaxations. Roe and Tonelli,[22] however, calculated one part of the vibrational contribution due to the freezing-in of the torsional oscillations of the chain backbone bonds. For a number of polymers, including polystyrene, it appeared that the sum of this term and the aforementioned contributions ΔC_1^{conf} and ΔC_1^{fv} is, although still smaller, close to the observed incremental change in specific heat.

Recently, DiMarzio and Dowell[23] also introduced a contribution due to the change in vibrational frequencies into the Gibbs–DiMarzio theory. They claim an average agreement within 20% between predicted and observed values of ΔC_{p_1} for various polymers. However, the values they attribute to the configurational contribution arising from the freezing-in of the free volume are much larger than those following from the original Gibbs–DiMarzio theory.

The foregoing analysis shows that the incremental change in specific heat results largely from the freezing-in of the conformational population, the torsional oscillations of the backbone, and the free volume. From this it is clear that the introduction of cross-links reduces the fraction of chain units that contribute to ΔC_{p_1}. The mobility of the latter units decreases also, but as stated before, we will assume that those degrees of freedom of these units that are frozen in at the glass transition remain, as a first approximation, the same. They can, in particular, still be in a trans or a gauche state (cf. ref 24). A higher glass transition temperature, therefore, results in a larger fraction of chain units in a gauche state. According to O'Reilly,[13] the contribution to ΔC_{p_1} arising from the freezing-in of the conformational population, the first term of eq 11, is approximately inversely proportional to the freezing-in temperature. The dependence of this contribution on the degree of cross-linking is therefore completely determined by the dependence of the glass transition temperature on the degree of cross-linking. For the other contributions, the situation is much more complicated. However, Simha and Boyer[25,26] presented arguments that for non-cross-linked polymers the product $\Delta C_{p_1} T_{g_1}$ is approximately constant. For cross-linked polymers this remains equally valid, provided ΔC_{p_1} is taken to be the incremental change in specific heat per mole of units capable of being activated, i.e., $\Delta C_{p_1}^{act}$. The foregoing analysis indicates that instead of assuming that $\Delta C_{p_1}^{act}(X)$ is independent of X, it is more reasonable to assume the following:

$$\Delta C_{p_1}^{act}(X) T_{g_1}(X) = \Delta C_{p_1}(X=0) T_{g_1}(X=0) \quad (12)$$

With this assumption eq 6 becomes

$$[dT_g(X)/dx_2]_{x_2=0} = \frac{\Delta C_{p_2}}{\Delta C_{p_1}(X=0)} \frac{T_{g_1}(X)}{T_{g_1}(X=0)}[T_{g_1}(X) - T_{g_2}] \quad (13)$$

This is the basic equation for the application of the Couchman–Karasz approach to polymer network/diluent systems, the validity of which will again be demonstrated for the styrene/divinylbenzene cross-linked polymers using ethylbenzene as a diluent.

Application

Equation 12 enables us to obtain $\Delta C_{p_1}^{act}(X)$ as a function of the degree of cross-linking. The results for the above-mentioned systems are presented in the third column of Table III. A comparison with the experimental data for $\Delta C_{p_1}(X)$ gives an estimation for the fraction of chain units f^{act} capable of being activated. Values for the fraction of units excluded from the glass transition, $f^{exc} = 1 - f^{act}$, are

Table III[a]

% DVB (w/w)	f^{exc}, %	$\Delta C_{p_1}^{act}$, J/(g K)	$(dT_g/dx_2)_{x_2=0}$, K/% dil		
			eq 10	eq 13	exptl
0	0	0.283	6.7	6.7	6.5
5	9	0.279	6.9	7.0	6.5
21	24	0.262	7.5	8.1	8
35.7	61	0.245	8.2	9.5	10

[a] Experimental data; see ref 7.

presented in the second column of Table III. They look very reasonable. In particular, the large value of 61% for the highly cross-linked sample is illustrative of the property that meshes containing less than four carbon atoms are largely excluded from activation. A percentage of 35% divinylbenzene implies an average mesh width of about three carbon atoms. The fact that 39% of the chain units can still be activated results primarily from the nonuniformity of the mesh lengths and other network imperfections.

The depression of the glass transition temperature of the different styrene/divinylbenzene networks by small amounts of ethylbenzene can easily be calculated from eq 13. The results are presented in column 5 and the agreement with the experimental values is within experimental error. For completeness, column 4 contains the calculated values using eq 10. They show a much smaller sensitivity for cross-linking. This clearly supports the viewpoint that the inverse proportionality of $\Delta C_{p_1}^{act}(X)$ to temperature is a much better approximation than the assumption, underlying eq 10, that $\Delta C_{p_1}^{act}(X)$ is independent of temperature. The enhanced sensitivity of the glass transition temperature of cross-linked polymers to small amounts of diluent is therefore due to both the increase of $T_{g_1}(X)$ and the decrease of $\Delta C_{p_1}^{act}(X)$. The latter, however, decreases much less than the observed incremental change in specific heat ΔC_{p_1}.

In the first section we assumed that the extrapolated change in specific heat ΔC_{p_2} of the diluent is inversely proportional to the temperature in the temperature range above T_{g_2}. If one assumes the same to be valid for the non-cross-linked polymer in the temperature range below T_{g_1}, eq 2 results in

$$T_g = \frac{x_1 \Delta C_{p_1} T_{g_1} + x_2 \Delta C_{p_2} T_{g_2}}{x_1 \Delta C_{p_1} + x_2 \Delta C_{p_2}} \qquad (14)$$

A similar relation has previously been derived by Gordon et al.[27] within the framework of the Gibbs–DiMarzio theory. Couchman and Karasz[1] also derived it using the classical thermodynamic theory outlined in the first section. The latter derivation, however, suggests a very restrictive applicability. The obvious extension of eq 14 to polymer networks is given by

$$T_g(X) = \frac{x_1 \Delta C_{p_1}^{act}(X) T_{g_1}(X) + x_2 \Delta C_{p_2} T_{g_2}}{x_1 \Delta C_{p_1}^{act}(X) + x_2 \Delta C_{p_2}} \qquad (15)$$

Using this expression and the values of $\Delta C_{p_1}^{act}(X)$ presented in column 3 of Table III, we have calculated the glass transition temperature depression for various amounts of ethylbenzene. Figure 1 shows that the agreement with the experimental values is good.

For the system with the highest degree of cross-linking the predicted depression is somewhat smaller than the observed one, implying that the actual value of $\Delta C_{p_1}^{act}$ is lower than the calculated one based on eq 12. This equation is based on the assumption that the number of degrees of freedom, which are frozen in at T_g, of those units which can be activated remain the same for different degrees of cross-linking. For a high degree of cross-linking it seems likely that there is also a reduction in the number of degrees of freedom, resulting in a lower $\Delta C_{p_1}^{act}$.

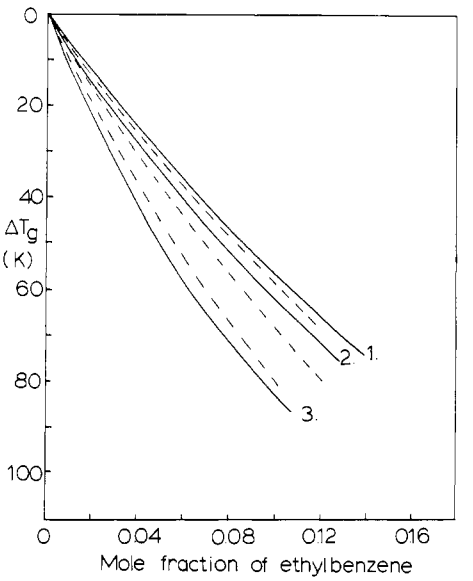

Figure 1. Comparison of the depression of T_g by ethylbenzene determined experimentally with that predicted by eq 15 for polystyrene (1) and two styrene/divinylbenzene networks: (2) 21.0% DVB; (3) 35.7% DVB. (—) Experimental, (---) theory.

Concluding Remarks

It has been demonstrated that the classical thermodynamic theory that worked so well in predicting mixture T_g's for some polymer blends works equally well for at least one polymer network/diluent system. The application to polymer networks is based on the assumption that the main effect of cross-linking is to reduce the number of chain units which can be thermally activated. Moreover, these chain units are the only ones involved in the observed glass transition temperature depression by diluents. For not too high degrees of cross-linking, the observed decrease of ΔC_{p_1} is primarily due to this reduction. A smaller part arises from the higher glass transition temperature and from a decrease of the number of degrees of freedom of the activated units. At a very high degree of cross-linking, ΔC_{p_1} becomes vanishingly small and the glass transition can no longer be observed by a DSC scan. It is, however, still possible to detect a T_g using dynamic mechanical measurements. The foregoing analysis shows that one should expect a much larger depression of the T_g of such a system by small amounts of diluent than for the systems discussed in this paper.

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Registry No. Divinylbenzene–styrene copolymer, 9003-70-7.

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Method for Estimating the Entropy of Macromolecules with Computer Simulation. Chains with Excluded Volume

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ABSTRACT: An approximate method for estimating the entropy of macromolecules with computer simulation is developed and applied preliminarily to relatively short ($N \leq 49$) self-avoiding walks (SAWs) on a 3-choice square lattice and a 5-choice simple-cubic lattice. The accuracy of S_{EV}, the contribution of the excluded volume (EV) effect to the entropy, is estimated for both lattices to be better than 1%. However, when the SAWs are confined within a "box", additional long-range contacts are formed and the estimated accuracy of S_{EV} becomes not better than 2–7%. We discuss ways to improve the accuracy of the method and explain how it can be extended to polymer models with EV and finite interactions (attractive or repulsive) as well.

Introduction

Calculation of the entropy of systems with short-range interactions (e.g., simple liquids) by means of computer simulation is not trivial[1–6] and becomes very difficult for macromolecules, where long-range interaction prevails. Gō and Scheraga[7,8] developed a method (based on normal coordinate analysis) for calculating the conformational entropy of macromolecules undergoing small (i.e., harmonic) fluctuations around their stable state (e.g., the α-helical state of a polypeptide) and applied it to several short polypeptides.[9,10] They also calculated[7] the entropy of a polypeptide in its random coil state at the Θ point,[11,12] i.e., neglected the excluded volume effect (see also ref 13). Recently, Karplus and Kushick[14] suggested calculating the covariances of the internal coordinates directly from the molecular dynamics or Monte Carlo simulation rather than performing normal coordinate analysis and applied their method to the molecular dynamics simulation of decaglycine and butane. These approximate treatments cover only the two extreme cases of very small and very large conformational fluctuations and are not applicable to states with intermediate chain flexibility.

In the present work, we develop a different procedure for estimating entropy, which, in principle, can be applied to *any* macromolecular state simulated with *any* computer simulation technique.[15–18] In this preliminary study, however, we apply the method to a relatively simple model, the self-avoiding walks (SAWs) (or chains with excluded volume (EV)) simulated with the direct Monte Carlo (DMC) procedure[19] on a square and a simple-cubic (SC) lattice. To model the strong, long-range, attractive interactions in a protein molecule, for example, we also confine the chains within a small "box" of varying size. Because of "sample attrition",[15] we were able to study with DMC only short SAWs of $N \leq 49$ (where N is the number of links in a walk). However, the DMC procedure enables us to obtain accurate estimates for the entropy using an asymptotically exact formula and thereby to examine the accuracy of our results. Our results are also compared to estimates for the entropy obtained with series expansion, and we also discuss how to extend our method to self-interacting SAWs.

Theory

Direct Monte Carlo. Self-avoiding walks of N steps with equal probability can be generated on a lattice by successively selecting random steps until a walk of N steps has been constructed or until double occupancy occurs at some lattice site; in this case the process stops and a new walk is started. This procedure, known as direct Monte Carlo (DMC),[19] is very inefficient for generating samples of long walks. It is due to the law of sample attrition, saying that the ratio of walks of N steps that avoid self-intersection, W_N, to the total number of walks started, W_0, constitutes a fraction decreasing exponentially with N.[15] However, this ratio enables one to estimate the entropy. The following relation holds:

$$W_N/W_0 \cong C_N/q(q-1)^{N-1} \tag{1}$$

where q is the lattice coordination number (reverse steps are forbidden) and C_N is the total number of possible SAWs of N links starting from a given point. The entropy S is[20,21]

$$S = k_B \log C_N \cong k_B[\log q + (N-1)\log(q-1) + \log(W_N/W_0)] \tag{2}$$

where k_B is the Boltzmann constant. The first two terms in eq 2 define S_I, the entropy of an ideal chain without EV

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